

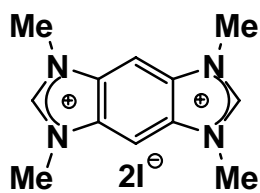
Dynamic Covalent Polymers Based Upon Carbene Dimerization

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Supplementary Material

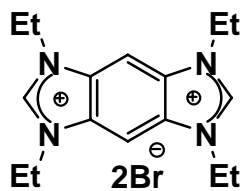
General Considerations. All reactions were performed under an atmosphere of nitrogen or inside of a nitrogen-filled drybox. ^1H and ^{13}C NMR spectra were recorded using a Varian Unity Plus (400 or 300 MHz) spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) downfield from tetramethylsilane using the residual protonated solvent as an internal standard (CDCl_3 , ^1H : 7.24 ppm and ^{13}C : 77.0 ppm; $(\text{CD}_3)_2\text{SO}$, ^1H : 2.49 and ^{13}C : 39.5 ppm; C_6D_6 , ^1H : 7.15 and ^{13}C : 128.0). Coupling constants (J) are expressed in Hertz (Hz). Where appropriate, descriptions of signals include singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). ^{13}C -NMR spectra were routinely run with broadband ^1H decoupling. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 or a VG analytical ZAB2-E instrument and are reported as m/z (relative intensity). UV-vis spectra were recorded using a Perkin Elmer Instruments Lambda 35 spectrometer. GPC data was obtained using an Waters HPLC system (1515 pump with a 2414 refractive index detector) with three Waters Styragel HR 1 columns thermostatted at 40 °C; molecular weight data is reported relative to polystyrene standards in DMF. PhCH_3 and benzene were distilled from CaH_2 or sodium and benzophenone under nitrogen atmosphere prior to use. DMF was used from a solvent purification column under an atmosphere of argon. Benzobisimidazole, [5,5']-bibenzimidazole, 1,1',3,3'-tetrabutylbenzobisimidazolium bromide (**2•Bu**), and 1,1',3,3'-tetrabutyl-5,5'-bibenzimidazolium bromide (**3•Bu**) were prepared as previously reported.¹ **1•Et'** was prepared according to literature procedures.²



1,1',3,3'-Tetramethylbenzobisimidazolium Diiodide (2•Me). Under a positive pressure of nitrogen, a flame dried 100 mL Schlenk tube was charged with NaH (60 wt %, 28 mg, 0.7 mmol), PhCH_3 (10 mL), benzobisimidazole (50 mg, 0.31 mmol), and a stir bar. The tube was sealed and the solution was stirred at 110 °C for 1 h and then allowed to cool to ambient temperature. Iodomethane (0.11 mL, 1.8 mmol) was then added via syringe under a positive pressure of nitrogen. The reaction vessel was then stirred at 110 °C for 1 h. After cooling to ambient temperature, dry DMF (10 mL) was added via syringe and the reaction was stirred at 110 °C for 6 h and then 60 °C for 4 h. Afterward, the resulting suspension was allowed to cool to ambient temperature and diluted with PhCH_3 (50 mL) which caused solids to precipitate. The solids were collected by vacuum filtration, rinsed with hexanes and ethyl acetate, and then dried under high vacuum to afford 100 mg (70% yield) of the desired product as a tan powder. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.91 (s, 2H), 8.84 (s, 2H), 4.17 (s, 12H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 146.6, 130.6, 98.5, 54.4.

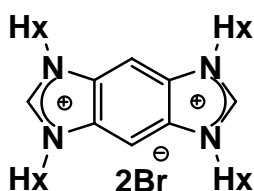
¹ Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496.

² Y. Liu, P. E. Lindner and D. M. Lemal, *J. Am. Chem. Soc.* 1999, **121**, 10626.



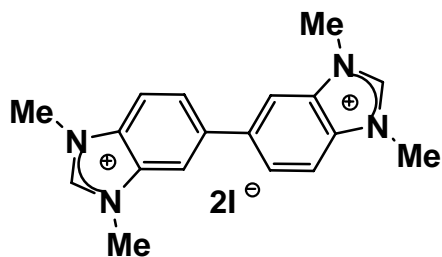
1,1',3,3'-Tetraethylbenzobisimidazolium Dibromide (2·Et). Under a positive pressure of nitrogen, a flame dried 100 mL Schlenk tube was charged with NaH (60 wt %, 50 mg, 1.2 mmol), PhCH₃ (20 mL), benzobisimidazole (100 mg, 0.6 mmol), and a stir bar. The reaction vessel was sealed and the solution was then stirred at 110 °C for 1 h and then allowed to cool to ambient temperature. Bromoethane (0.3 mL, 3.6 mmol)

was then added via syringe and the resulting suspension was stirred at 110 °C for 1 h. After cooling to ambient temperature, dry DMF (15 mL) was added via syringe and the reaction was stirred at 110 °C for 12 h. The resulting solution was then allowed to cool to ambient temperature and then diluted with PhCH₃ (50 mL) which caused solids to precipitate. The solids were then collected by vacuum filtration, rinsed with hexanes and dried under high vacuum to afford 150 mg (55% yield) of the desired product as a tan powder. ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.12 (s, 2H), 8.99 (s, 2H), 4.63 (m, *J* = 7.2 Hz, 8H), 1.61 (t, *J* = 7.2 Hz, 12H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 145.1, 130.7, 99.2, 43.4, 14.4.



1,1',3,3'-Tetrahexylbenzobisimidazolium Dibromide (2·Hx). Under a positive pressure of nitrogen, a flame dried 100 mL round bottom flask was charged with NaH (60 wt %, 28 mg, 0.7 mmol), PhCH₃ (10 mL), benzobisimidazole (50 mg, 0.31 mmol), and stir bar. The flask was then equipped with reflux condenser and placed under an atmosphere of nitrogen. The solution was then stirred at 110 °C for 1 h and then allowed

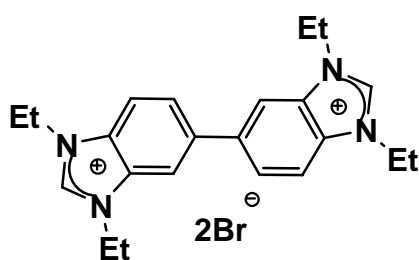
to cool to ambient temperature. 1-Bromohexane (0.26 mL, 1.8 mmol) was then added via syringe and the reaction vessel was then stirred at 110 °C for 1 h. After cooling to ambient temperature, dry DMF (10 mL) was added via syringe and the reaction was re-heated at 110 °C for 6 h and then 60 °C for 4 h. Afterward, the resulting suspension was allowed to cool to ambient temperature, diluted with PhCH₃ (50 mL) which caused solids to precipitate. The solids were collected by vacuum filtration, rinsed with hexanes and then dried under high vacuum to afford 183 mg (90% yield) of the desired product as a tan powder. ¹H NMR (400 MHz, benzene-*d*₆): δ 10.37 (s, 2H), 9.24 (s, 2H), 4.64 (br, 8H), 1.95 (br, 8H), 1.26 (br, 24H), 0.816 (t, *J* = 6.4 Hz, 12H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 146.2, 130.8, 100.0, 48.1, 31.4, 29.0, 26.0, 22.6, 14.5.



1,1',3,3'-Tetramethyl-5,5'-bibenzimidazolium Diiodide (3·Me). Under a positive pressure of nitrogen, a 100 mL Schlenk tube was charged with NaH (60 wt %, 75 mg, 2 mmol), PhCH₃ (20 mL), [5,5']-bibenzimidazole (234 mg, 1 mmol), and a stir bar. The resulting solution was stirred at 110 °C for 1 h and then allowed to cool to ambient temperature. Iodomethane (0.37 mL, 6 mmol) was then added via syringe and the resulting suspension was stirred at

110 °C for 1 h. After cooling to ambient temperature, dry DMF (20 mL) was added via syringe and the resulting solution was heated to 110 °C for 6 h and then 60 °C for 4 h. Afterward, the resulting suspension was allowed to cool to ambient temperature and then diluted with PhCH₃ (50 mL) which caused solids to precipitate. The solids were collected by vacuum filtration, rinsed with hexanes and ethyl acetate, and dried under high vacuum to afford 160 mg (30% yield) of the desired product as a tan powder. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.69 (s, 2H),

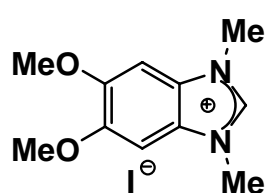
8.52 (s, 2H), 8.2 (m, 4H), 4.1 (d, 12H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 138.3, 133.1, 132.1, 126.8, 114.7, 112.6, 33.9; HRMS calcd for $\text{C}_{18}\text{H}_{22}\text{N}_4$ $[\text{M}+\text{H}^+]$ 291.160972, found 291.161471.



1,1',3,3'-Tetraethyl-5,5'-bibenzimidazolium Dibromide

(3·Et). Under a positive pressure of nitrogen, a flame dried 100 mL Schlenk tube was charged with NaH (60 wt %, 80 mg, 2 mmol), PhCH_3 (30 mL), [5,5']-bibenzimidazole (234 mg, 1 mmol), and a stir bar. The reaction vessel was then sealed and the solution was stirred at 110 °C for 1 h. After cooling to ambient temperature, bromoethane (0.5 mL, 6 mmol) was added via syringe. The resulting suspension was then stirred at

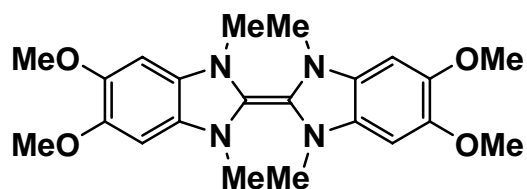
110 °C for 1 h and cooled to ambient temperature. Dry DMF (30 mL) was then added via syringe and the reaction vessel was stirred at 110 °C for 6 h and then 60 °C for 4 h. Afterward, the resulting suspension was cooled to ambient temperature and then diluted with PhCH_3 (50 mL) which caused solids to precipitate. The solids were collected by vacuum filtration, rinsed with hexanes, and dried under high vacuum to afford 360 mg (50% yield) of the desired product as a tan powder. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 9.92 (s, 2H), 8.60 (s, 2H), 8.23 (m, 4H), 4.59 (m, 8H), 1.58 (m, 12H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 142.1, 138.6, 132.4, 131.5, 127.1, 114.8, 112.7, 43.0, 42.9, 14.7, 14.6; HRMS calcd for $\text{C}_{22}\text{H}_{30}\text{N}_4$ $[\text{M}+\text{H}^+]$ 347.223572, found 347.223733.



5,6-Dimethoxy-1,3-Dimethylbenzimidazolium Diiodide.

Under a positive pressure of nitrogen, a flame dried 100 mL Schlenk tube was charged with NaH (60 wt %, 178 mg, 4.45 mmol), 5,6-dimethoxy benzimidazolium formate (490 mg, 2.21 mmol), and a stir bar. Dry, degassed DMF (40 mL) was then added and the resulting solution was stirred at ambient temperature for 15 min. Excess iodomethane (0.41 mL,

6.63 mmol) was then added under a positive flow of nitrogen and the reaction vessel was sealed and stirred at 60 °C for 24 h. After cooling to ambient temperature, PhCH_3 (20 mL) was added to the solution which caused solids to precipitate. The solids were collected by filtration and rinsed with excess PhCH_3 . The collected solids were then vigorously stirred in refluxing ethyl acetate and hot-filtered to remove residual $\text{NaI}\cdot\text{DMF}$ and then dried under high vacuum to afford 420 mg (57% yield) of the desired product as a white powder. ^1H NMR (300 MHz, $\text{DMSO-}d_6$): δ 9.41 (s, 1H), 7.5 (s, 2H), 4.0 (s, 6H), 3.89 (s, 6H); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 149.4, 140.1, 125.5, 95.3, 56.5, 33.4.



5,6-Dimethoxy-1,3-Dimethylbenzimidazolylidene

Dimer (6): Under a positive pressure of nitrogen, a flame dried 5 mL vial was charged with 5,6-

dimethoxy-1,3-dimethylbenzimidazolium iodide (100 mg, 0.29 mmol), NaH (60 wt %, 15 mg, 0.58 mmol), *t*BuOK (1 mg, 0.01 mmol), and a stir bar. The reactants

were then suspended in benzene- d_6 (2 mL) and the vial was sealed with a Teflon lined cap. The resulting slurry was stirred for 12 h at ambient temperature and then filtered using a 0.2 μm Whatman PTFE filter to afford a vibrant yellow solution. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 6.32 (s, 4H), 3.61 (s, 12H), 2.75 (s, 12H).

Representative polymerization procedure: 1,1',3,3'-Tetraethyl-5,5'-bibenzimidazolium bromide (**3·Et**) (150 mg, 0.20 mmol), NaH (95 wt %, 15 mg, 0.60 mmol), *t*BuOK (1 mg, 0.01 mmol), and a magnetic stir bar were added to a vial in a N₂-filled drybox. The reactants were then suspended in benzene-*d*₆ (1 mL) and the vial was capped with a Teflon-lined septum. Under vigorous stirring, the resulting slurry was stirred at room temperature for 12 h. The mixture was then filtered through a 0.2 μm Whatman PTFE filter which afforded a dark red solution. This solution was either analyzed directly or poured into a large volume (> 10 mL) of dry, degassed pentane (under an atmosphere of N₂) to precipitate polymer which was collected by filtration. Note: these materials oxyluminesce upon exposure to oxygen and ultimately decompose to the respective cyclic urea(s).